Dodecanuclear Zirconium Precursor Enables Green and Rapid Mechanosynthesis of High-Porosity NU- and UiO-type Metal-Organic Frameworks

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The use of a dodecanuclear zirconium acetate cluster as a precursor enables the rapid, clean mechanochemical synthesis of high-microporosity metal-organic frameworks NU-901 and UiO-67, with surface areas up to 2250 m² g⁻¹. Real-time X-ray diffraction monitoring reveals that mechanochemical reactions involving the conventional hexanuclear zirconium methacrylate precursor are hindered by the formation of an inert intermediate, which does not appear when using the dodecanuclear acetate cluster as a reactant.

Metal-organic frameworks (MOFs) are modular porous materials[1-3] with proposed or commercial[3c] uses in gas storage and separation,[4] catalysis,[5] degradation of harmful agents,[6] functional thin films,[7] electrochemical[8] and molecular sensing,[9] light harvesting[10] and others. MOFs based on cationic $[Zr_6O_4(OH)_4^{12+}]$ ("Zr_6", Fig. 1d) clusters[11] are particularly intriguing as they combine high porosity[11e] and catalytic activity[12] with excellent resistance to water, high temperatures and pH.[13] Among different techniques for MOF synthesis,[14] mechanochemistry has emerged as a rapid, clean approach to synthesise a wide range of popular MOFs at room temperature,[15] without resorting to bulk solvents or auxiliary reagents. Whereas mechanochemistry has been successfully used to synthesise a number of popular MOFs, including pillared MOFs,[16] IRMOFs,[17] MOF-74,[18] HKUST-1,[19] metal azolate frameworks[20] and UiO-66 derivatives[21] such work has remained limited to materials involving di- or tritopic linkers based on a single aromatic ring, with porosities between 500-1500 m^2g^{-1}. Consequently, the ability of mechanochemistry to access MOFs of high microporosity, based on complex, larger ligands, has remained unexplored.

We now describe the use of mechanochemistry for the synthesis of the highly porous *scu*-topology NU-901[11f] MOF, based on the tetratopic ligand 1,3,6,8-*tetrakis*(*p*-benzoic acid)pyrene, (H_4**TBAPY**, Fig. 1). Whereas this is the first entry of mechanochemistry into the assembly of MOFs based on complex linkers, it is also the first example of a NU-type MOF synthesised by a solvent-free route. In addition, we show the mechanochemical assembly of an *fcu*-topology UiO-67[11a,11c] framework with a Brunauer-Emmet-Teller (BET) surface area of 2250 $m^2\ g^{-1}$, demonstrating the ability of mechanochemistry to generate materials with very high microporosity. Central to these mechanochemical advances is the use of a dodecanuclear zirconium acetate cluster **1** as a precursor (Fig. 1a).

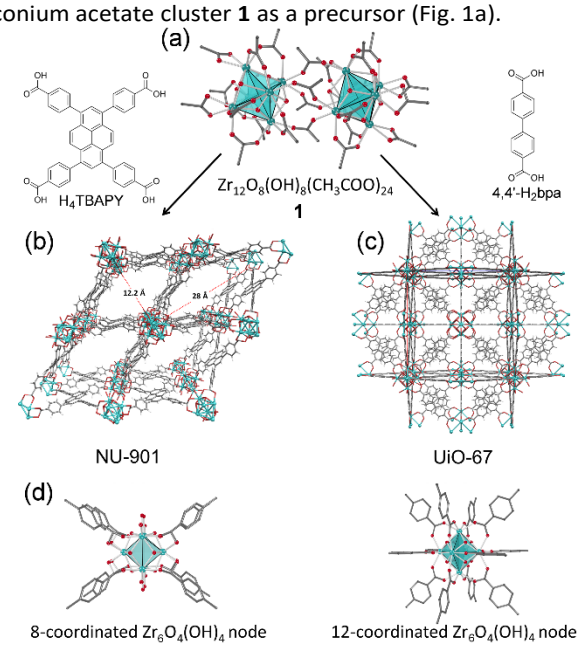

Figure 1. a) the Zr_{12} acetate oxocluster **1**. Milling of **1** with tetratopic or ditopic ligands results in rapid formation of: b) NU-901 or c) UiO-67 MOFs. d) Different modes of binding of ligands to the Zr_6 node in each respective MOF.

Our initial attempt to mechanochemically synthesize a NU-type MOF was based on the liquid-assisted grinding (LAG) procedure previously used to synthesize the terephthalate-based UiO-66, by milling the carboxylic acid ligand with either the benzoate or the methacrylate-based (**2**) Zr_6 clusters as precursors.[21a] While milling with benzoate precursor produced only a mixture of reactants, subsequent aging of the mixture in a N,N-dimethylformamide (DMF) atmosphere yielded NU-901, which was characterised by powder X-ray diffraction (PXRD), and exhibited a BET surface of 1250 m^2g^{-1} after activation. *In situ* synchrotron PXRD monitoring of the milling reaction of **2** and H_4**TBAPY** in stoichiometric ratio 1:2 revealed immediate appearance of NU-901 (see ESI),[11f] concomitant to the gradual loss of H_4**TBAPY**. After 45 min, PXRD pattern of the reaction mixture exhibited only signals of NU-901. However, the product was a sticky solid, difficult to remove from the vessel, with moderate BET surface area after activation (450-900 m^2g^{-1}, ESI).

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Electronic Supplementary Information (ESI) available: Synthetic procedures, selected PXRD, FTIR-ATR, porosity, TGA and SEM data. See DOI: 10.1039/x0xx00000x

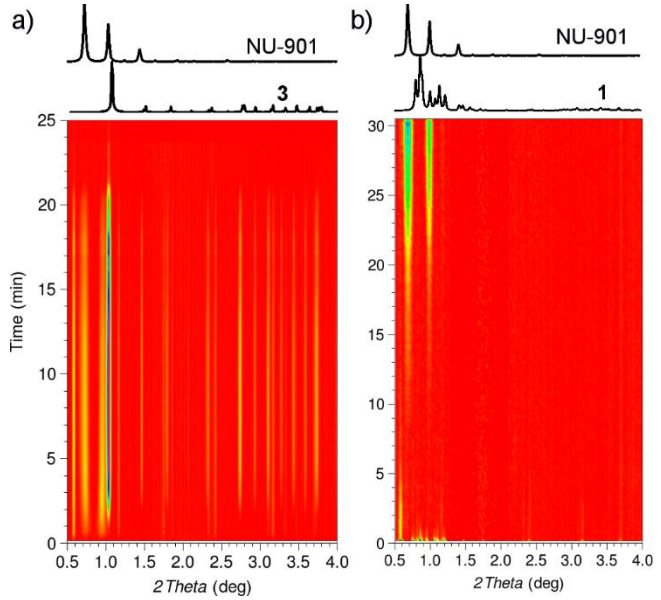

Figure 2. *In situ* synchrotron PXRD monitoring of mechanochemical synthesis of: a) NU-901 from **2**, showing the concomitant formation of **3** and NU-901. The reaction mixture stuck to the wall of the vessel after ca. 20 minutes of milling, resulting in a disappearance of diffraction signal; and b) NU-901 from **1**. Simulated PXRD patterns are shown above.

Monitoring the milling reaction of **2** and H_4**TBAPY** in the 1:1 stoichiometric ratio revealed the appearance of another set of X-ray reflections, that could not be matched to any known MOFs involving zirconium nodes and H_4**TBAPY**-based linkers (Fig. 2). Further work revealed that the signals correspond to a new phase (**3**), which was also obtained as a pure material by 5 minutes milling of **2** with DMF, even in the absence of H_4**TBAPY** (see ESI). Compound **3** was subsequently isolated and identified as a new Zr_6 cluster with a structure significantly different from **2** (Figs. 3 and ESI). In contrast to Zr_6-clusters that are decorated by 12 carboxylate ligands, the cluster in **3** involves a total of 16 ligands, including 12 carboxylates and four DMF molecules. The six Zr atoms in **3** form a distorted octahedron of S_4 symmetry, unlike the C_3 symmetry present in **2** (CSD code REBNUH). The main difference between the clusters of **2** and **3** is in coordination of the ancillary ligands. In **2**, three methacrylate ligands chelate the zirconium cations, whereas the remaining nine act as bridging ligands in the Zr_6 core. In **3**, no chelating ligands are present; from the 12 methacrylate anions, eight are bridging and four are coordinated in a monodentate fashion (two on each Zr atom positioned on the S_4 axis), with each free carboxylate oxygen stabilized by hydrogen bonding to one of the μ_3-OH groups of the oxo-zirconium core (d(O···O) = 2.7632(3) Å, Fig. 3). The coordination sphere of the remaining four Zr cations is completed by a DMF molecule, thus introducing four ancillary ligands onto the Zr_6 core. Importantly, **3** appears to be a hindrance in the mechanosynthesis of NU-901, as it persists in the reaction mixture and appears before H_4**TBAPY** is consumed (see ESI).

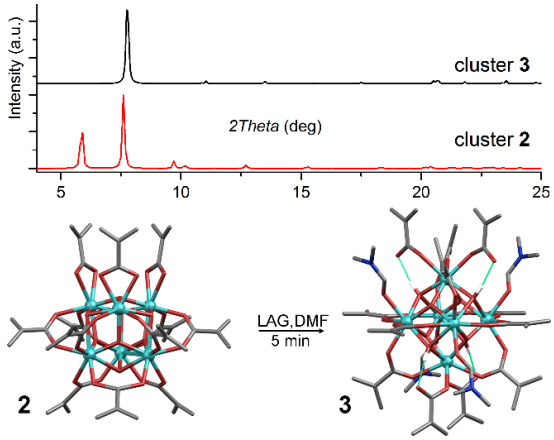

Figure 3. Mechanochemical transformation of the 12-coordinated Zr_6 cluster **2** (left) into a 16-coordinated cluster **3** by LAG using DMF. The PXRD data for each cluster is presented at the top. Hydrogen atoms, except those on the cluster core, are omitted for clarity. Hydrogen bonds are shown as green dotted lines.

Next, we explored the synthesis of NU-901 using a dodecanuclear oxo-bridged zirconium acetate cluster **1** (Figs. 1a and ESI), with the same core as the one recently reported in solvothermal synthesis of new Zr_{12} and Zr_6 MOFs.[22] Real-time PXRD monitoring of the milling reaction of **1** and H_4**TBAPY** revealed rapid formation of NU-901, and complete disappearance of reactants within 30 minutes (Fig. 2). In this case, the sample remained a free-flowing powder that was readily removed from the reaction vessel. Whereas PXRD indicated quantitative conversion, in order to ensure purity, the product was rapidly washed with a minimal amount of DMF. The sample after activation exhibited a BET area of 1610 $m^2\ g^{-1}$, matching well to reported values for NU-901 (see ESI).[23]

The significant improvement in mechanosynthesis of NU-901 upon using the dodecanuclear precursor **1** led us to explore its use in the mechanosynthesis of UiO-67, an *fcu* zirconium MOF based on the extended ligand biphenyl-4,4'-dicarboxylic acid (H_2**BPA**, Fig. 1). Mechanosynthesis of UiO-67 was recently described by the Lamaty group, by milling of H_2**BPA** with the methacrylate precursor **2**, yielding a material with BET surface area of 750 $m^2\ g^{-1}$.[24] Our attempts to use **2** as the precursor gave similar results, with porosity ranging from 380 to 1165 m^2g^{-1}, possibly due to methacrylate impurities trapped in UiO-67. Whereas the BET areas of the MOF could be increased to 1740 m^2g^{-1} by aging for a week at 45 °C in DMF vapor, the samples still appeared poorly crystalline by PXRD (see ESI).

In contrast, LAG of **1** and 4,4'-H_2**BPA** in the required 1:12 stoichiometric ratio, and using DMF as liquid additive, led to rapid formation of highly crystalline UiO-67). After activation, the purified UiO-67 exhibited an outstanding BET area of 2250 $m^2\ g^{-1}$ (see ESI). Whereas this surface area exceeds any previously reported ones for UiO-67, it is also the highest so far reported BET area for a mechanochemically prepared MOF. Importantly, the nitrogen sorption isotherm indicates a high level of ordering in the MOF structure, with a low fraction of missing linker defects, which was also corroborated by thermogravimetric analysis (TGA) showing average of 5.5 ligands per Zr_6 node (see ESI). Consequently, the synthesis of UiO-67 from precursor **1** demonstrates the ability to synthesize

materials with very high microporosity and high crystallinity using mechanochemistry.

In situ monitoring of the LAG mechanosynthesis of UiO-67 also revealed different reaction pathways dependent on the choice of precursor cluster. LAG reaction of **2** with 12 equivalents of 4,4'-H_2**BPA** in presence of DMF revealed almost immediate formation of **3**, which remained stable for 90 minutes milling, without appearance of UiO-67. The formation of UiO-67 was observed only upon longer, more intense milling (ESI). We surmise that **3** is a less reactive form of the Zr_6 cluster, which interferes with the formation of zirconium MOFs in DMF, which may also explain the poorer yields and crystallinity previously reported for UiO-66 MOFs prepared from **2** by LAG with DMF.[21a]

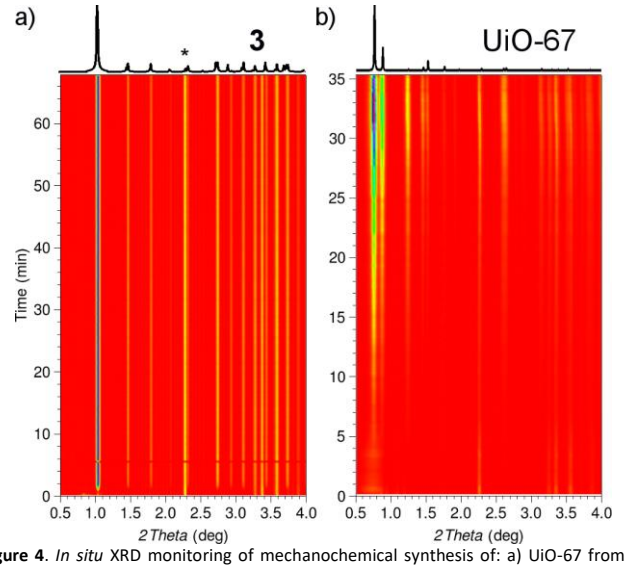

Figure 4. *In situ* XRD monitoring of mechanochemical synthesis of: a) UiO-67 from **2**, revealing immediate and exclusive formation of **3** which remains stable for almost 90 minutes milling; b) UiO-67 from **1**. The Bragg reflection at 2.25 *2theta* (*) belongs to 4,4'-H_2**BPA** reactant.

In contrast, *in situ* monitoring of the reaction involving **1** as the precursor led to immediate formation of UiO-67 after 5 minutes, with complete conversion after ≈35 minutes (Fig. 4).

The high crystallinity and outstanding BET area of UiO-67 mechanochemically generated from **1** led us to explore its activity as a heterogeneous catalyst in hydrolytic degradation of the nerve agent simulant dimethyl 4-nitrophenyl phosphate (DMNP, Fig. 5), standard compound in testing the Zr-MOFs hydrolytic activity.[6b] The UiO-67 sample prepared from **1** displayed high hydrolytic activity, 2.5 min for an initial half-life for degradation of DMNP, which is much faster than the popular and successful UiO-67 catalysts, made from solution ($t_{1/2}$(UiO-67) = 5 min). The importance of using **1** as the precursor is evident from the catalytic activity of UiO-67 mechanochemically prepared from **2** (Fig. 5), which exhibited an initial half-life of >20 minutes even for samples with a high BET surface area of 1750 $m^2\ g^{-1}$. The high catalytic activity of UiO-67 generated mechanochemically from **1** is likely to be facilitated by small particle size range of 40-80 nm, established by scanning electron microscopy (see ESI).

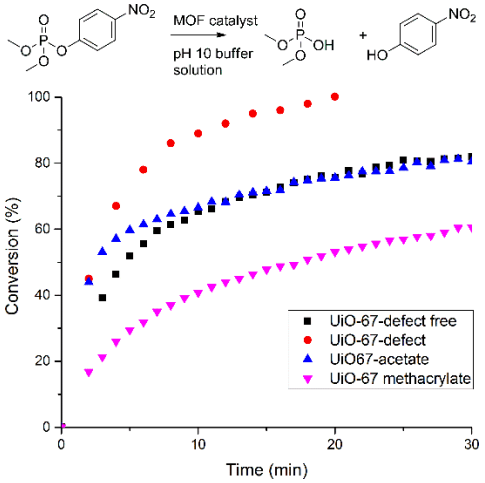

Figure 5. Hydrolysis of nerve agent simulant DMNP using UiO-67: a) reaction scheme and b) comparison of hydrolysis profiles in the presence of UiO-67 made solvothermally (black: low-defect phase; red: high-defect phase); mechanochemically from **1** (blue) and by milling and aging from **2** (magenta).

In summary, the use of a Zr_{12}-acetate cluster as a precursor enabled the rapid solvent-free synthesis of highly porous NU-901 and UiO-67 MOFs, in high yields and with minimum work-up requirements. The synthesis of these MOFs demonstrates the ability to use mechanochemistry for the synthesis of highly porous materials based on complex organic ligands, with the herein prepared UiO-67 representing the first example of a material with a BET surface area above 2000 $m^2\ g^{-1}$ obtained by ball milling. *In situ* monitoring revealed that mechanochemical formation of zirconium MOFs from the conventional hexanuclear methacrylate precursor is hindered by the appearance of a previously not reported inert Zr_6-cluster bearing ancillary DMF ligands. In contrast, the use of a dodecanuclear precursor does not lead to this phase, enabling rapid and direct synthesis of zirconium MOFs, even on gram scale. We are currently exploring further applications of such dodecanuclear clusters in mechanochemical reactions.

Conflicts of interest

There are no conflicts to declare.

Notes and references

Milling experiments were performed using Retsch MM400 or Insolido Technologies IST500 mixer mills. The reaction mixture (ca. 150 mg for NU-901 or ca. 300 mg for UiO-67) was milled using two stainless steel balls (1.4 grams each) for 30-180 minutes. *In situ* PXRD studies were done at the High Resolution Powder Diffraction Beamline P02.1 (DESY, Hamburg) using an unfocused, collimated X-ray beam of ca. 1 x 1 mm^2 size and a PerkinElmer 2D area detector.

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1 a) O. M. Yaghi, G. Li and H. Li, *Nature*, 1995, **378**, 703; b) S. Kitagawa, S. Kawata, Y. Nozaka and M. Munakata, *Dalton Trans*., 1993, 1399; c) R. Robson, *Dalton Trans.* 2008, 5113; d) H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 1230444.

2 a) T. Islamoglu, S. Goswami, Z. Li, A. J. Howarth, O. K. Farha and J. T. Hupp, *Acc. Chem. Res*., 2017, **50**, 805; b) W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, M. Bosch and H.-C. Zhou, *Chem. Soc. Rev*., 2014, **43**, 5561.

3 a) J. J. Perry IV, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev*., 2009, **38**, 1400; b) Z. Zhang and M. J. Zaworotko, *Chem. Soc. Rev*., 2014, **43**, 5444; c) *Nat. Chem.* 2016, **8**, 987.

4 a) M. S. Denny Jr, J. C. Moreton, L. Benz and S. M. Cohen, *Nat. Rev. Mater*., 2016, **1**, 16078; b) R. B. Getman, Y.-S. Bae, C. E. Wilmer and R. Q. Snurr, *Chem. Rev.*, 2012, **112**, 703; c) J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869; d) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724.

5 a) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; b) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev*., 2009, **38**, 1450; c) L. Zhu, X.-Q. Liu, H.-L. Jiang and L.-B. Sun, *Chem. Rev.*, 2017, **117**, 8129.

6 a) N. S. Bobbitt, M. L. Mendonca, A. J. Howarth, T. Islamoglu, J. T. Hupp, O. K. Farha and R. Q. Snurr, *Chem. Soc. Rev*., 2017, **46**, 3357; b) J. E. Mondloch, M. J. Katz, W. C. III, P. Ghosh, P. Liao, W. Bury, G. W. Wagner, M. G. Hall, J. B. DeCoste, G. W. Peterson, R. Q. Snurr, C. J. Cramer, J. T. Hupp and O. K. Farha, *Nat. Mater*., 2015, **14**, 512.

7 a) S. Sakaida, K. Otsubo, O. Sakata, C. Song, A. Fujiwara, M. Takata and H. Kitagawa, *Nat. Chem*., 2016, **8**, 377; b) A. Bétard and R. A. Fischer, *Chem. Rev.*, 2012, **112**, 1055.

8 a) L. Liu, Y. Zhou, S. Liu and M. Xu, *ChemElectroChem*, 2017, **5**, 6; b) H. Hosseini, H. Ahmar, A. Dehghani, A. Bagheri, A. Tadjarodi and A. R. Fakhari, *Biosens. Bioelectron.*, 2013, **42**, 426.

9 a) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105; b) B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian and E. B. Lobkovsky, *Adv. Mater*., 2007, **19**, 1693; c) S. Liu, Z. Xiang, Z. Hu, X. Zheng and D. Cao, *J. Mater. Chem*., 2011, **21**, 6649.

10 T. Zhang and W. Lin, *Chem. Soc. Rev*., 2014, **43**, 5982.

11 a) J. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850; b) M. Kandiah, M. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. Quadrelli, F. Bonino and K. Lillerud, *Chem. Mater*., 2010, **22**, 6632; c) M. J. Katz, Z. J. Brown, Y. J. Colon, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun*., 2013, **49**, 9449; d) T.-F. Liu, D. Feng, Y.-P. Chen, L. Zou, M. Bosch, S. Yuan, Z. Wei, S. Fordham, K. Wang and H.-C. Zhou, *J. Am. Chem. Soc.*, 2015, **137**, 413; e) T. C. Wang, W. Bury, D. A. Gómez-Gualdrón, N. A. Vermeulen, J. E. Mondloch, P. Deria, K. Zhang, P. Z. Moghadam, A. A. Sarjeant, R. Q. Snurr, J. F. Stoddart, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2015, **137**, 3585; f) C.-W. Kung, T. C. Wang, J. E. Mondloch, D. Fairen-Jimenez, D. M. Gardner, W. Bury, J. M. Klingsporn, J. C. Barnes, R. Van Duyne, J. F. Stoddart, M. R. Wasielewski, O. K. Farha and J. T. Hupp, *Chem. Mater*., 2013, **25**, 5012; g) R. Vakili, S. Xu, N. Al-Janabi, P. Gomez, S. M. Holmes, and X. Fan, *Microporous Mesoporous Mater.* 2018, **260**, 45.

12 a) P. Deria, D. A. Gomez-Gualdron, I. Hod, R. Q. Snurr, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2016, **138**, 14449; b) C. Wang, Z. Xie, K. E. de Krafft and W. Lin, *J. Am. Chem. Soc.*, 2011, **133**, 13445; c) H. Fei and S. M. Cohen, *Chem. Commun*., 2014, **50**, 4810.

13 a) N. C. Burtch, H. Jasuja and K. S. Walton, *Chem. Rev.*, 2014, **114**, 10575; b) P. Deria, Y. G. Chung, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Sci.*, 2015, **6**, 5172; c) J. E. Mondloch, M. J. Katz, N. Planas, D. Semrouni, L. Gagliardi, J. T. Hupp and O. K. Farha, *Chem. Commun*. 2014, **50**, 8944.

14 M. J. Van Vleet, T. Weng, X. Li and J. R. Schmidt, *Chem. Rev.,* 2018, **118**, 3681.

15 15. P. A. Julien, C. Mottillo and T. Friščić, *Green Chem*., 2017, **19**, 2729.

16 T. Friščić, D. G. Reid, I. Halasz, R. S. Stein, R. E. Dinnebier and M. J. Duer, *Angew. Chem. Int. Ed*., 2009, **49**, 712.

17 D. Prochowicz, K. Sokolowski, I. Justyniak, A. Kornowicz, D. Fairen-Jimenez, T. Friščić and J. Lewinski, *Chem. Commun*., 2015, **51**, 4032.

18 P. A. Julien, K. Užarević, A. D. Katsenis, S. A. J. Kimber, T. Wang, O. K. Farha, Y. Zhang, J. Casaban, L. S. Germann, M. Etter, R. E. Dinnebier, S. L. James, I. Halasz and T. Friščić, *J. Am. Chem. Soc.*, 2016, **138**, 2929.

19 a) T. Stolar, L. Batzdorf, S. Lukin, D. Žilić, C. Motillo, T. Friščić, F. Emmerling, I. Halasz and K. Užarević, *Inorg. Chem.*, 2017, **56**, 6599; b) W. Yuan, A. Garay, A. Pichon, R. Clowes, C. D. Wood, A. I. Cooper and S. L. James, *CrystEngComm*, 2010, **12**, 4063.

20 P. J. Beldon, L. Fábián, R. S. Stein, A. Thirumurugan, A. K. Cheetham and T. Friščić, *Angew. Chem. Int. Ed*., 2010, **49**, 9640; b) A. D. Katsenis, A. Puškarić, V. Strukil, C. Mottillo, P. A. Julien, K. Užarević, M.-H. Pham, T.-O. Do, S. A. J. Kimber, P. Lazić, O. Magdysyuk, R. E. Dinnebier, I. Halasz and T. Friščić, *Nat. Commun*., 2015, **6**, 6662.

21 a) K. Užarević, T. C. Wang, S.-Y. Moon, A. M. Fidelli, J. T. Hupp, O. K. Farha and T. Friščić, *Chem. Commun*., 2016, **52**, 2133; b) Y.-H. Huang, W.-S. Lo, Y.-W. Kuo, W.-J. Chen, C.-H. Lin and F.-K. Shieh, *Chem. Commun*., 2017, **53**, 5818.

22 A. A. Bezrukov, K. W. Tornroos, E. Le Roux and P. D. C. Dietzel, *Chem. Commun*., 2018, **54**, 2735.

23 P. Deria, J. Yu, T. Smith and R. P. Balaraman, *J. Am. Chem. Soc.*, 2017, **139**, 5973.

24 H. Ali-Moussa, R. Navarro Amador, J. Martinez, F. Lamaty, M. Carboni and X. Bantreil, *Mater. Lett*., 2017, **197**, 171.